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Production of Carbon Nanotubes by Different Routes—A Review

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Abstract

Carbon Nanotubes are one the most important materials of future. Discovered in 1991, they have reached a stage of attracting the interests of many companies world wide for their large scale production. They possess remarkable electrical, mechanical, optical, thermal and chemical properties, which make them a perfect "fit" for many engineering applications. In this paper various methods of production of carbon nanotubes are discussed outlining their capabilities, efficiencies and possible exploitation as economic large scale production methods. Chemical vapor disposition (CVD) is proposed as a potential method for economic large scale production of carbon nanotubes due to its relative simplicity of operation, process control, energy efficiency, raw materials used, capability to scale up as large unit operation, high yield and purity.

Keywords: Carbon Nanotubes, Chemical Vapor Deposition (CVD), Unit Operation, Yield

1. Introduction

Carbon nanotubes (CNTs) are allotropes of carbon. A carbon nanotube is a one-atom thick sheet of graphite (called graphene) rolled up into a seamless cylinder with diameter of the order of a nanometer. This results in a nanostructure where the length-to-diameter ratio exceeds 10,000. Such cylindrical carbon molecules have novel properties that make them potentially useful in a wide variety of applications in mechanical, structural, thermal, electrical & electronics, optical, biomedical and other fields of science, engineering & medicine. They exhibit extraordinary strength and unique electrical properties, and are efficient conductors of heat. Their name is derived from their size, since the diameter of a nanotube is on the order of a few nanometers (approximately 50,000 times smaller than the width of a human hair), while they can be up to several millimeters in length. [1,2].

Though discovered far earlier [3-5], first noticeable discovery of carbon nanotubes was reported by Ilijima [6] in 1991, when he found layers of carbo (graphene) rolled into tubular structure in the soot of arc dischage method. The nanotubes consisted of up to several tens of graphitic shells (so called multi-walled carbon nanotubes (MWNT)) with adjacent shell separation of 0.34 nm, diameters of 1 nm and high length/diameter ratio. Ilijima's discovery of carbon nanotubes in the insoluble material of arc-burned graphite rods created the buzz that greatly accelerated work on synthesis, production and properties of carbon nanotubes. It took two more years for Iijima and Ichihashi at NEC [7], and Bethune *et al*. [8] at IBM to synthesize SWNT by addition of transition metal catalysts to carbon in an arc discharge in 1993. Significant contributions to the race for devising method for production of carbon nanotubes were made by laser-ablation synthesis of bundles of aligned SWNT with small diameter distribution by Smalley and co- workers at Rice University in 1995 [9] and by catalytic growth of nanotubes by the chemical vapor decomposition (CVD) method by Yacaman *et al*. [10].

There are two main types of carbon nanotubes [11] that can have high structural perfection. Single walled nanotubes (SWNT), these consist of a single graphite sheet seamlessly wrapped into a cylindrical tube. Multi walled nanotubes (MWNT), these comprise an array of nanotubes one concentrically placed inside another like rings of a tree trunk.

2. Production of Carbon Nanotubes

There are various methods of production of carbon nanotubes such as production of nanotubes by arc discharge, chemical vapor deposition, laser ablation, flame synthesis, high pressure carbon monoxide (HiPco), electrolysis, pyrolysis etc. But they can be mainly classified into following groups.

1) Physical Processes
2) Chemical Processes
3) Miscellaneous Processes

2.1. Physical Processes

These are the processes, which make use of physical principles of carbon conversion into nanotubes. These include popular process of carbon nanotubes production such as arc discharge and laser ablation. Due to their wide spread popularity they are by far the most widely used processes for nanotubes production for experimental purposes.

2.1.1. Arc Discharge

This is one of the oldest methods of carbon nanotube production. First utilized by Iijima [6] in 1991 at NEC's Fundamental Research Laboratory to produce new type of finite carbon structures consisting of needle-like tubes. The tubes were produced using an arc discharge evaporation method similar to that used for the fullerene synthesis. The carbon needles, ranging from 4 to 30 nm in diameter and up to 1 mm in length, were grown on the negative end of the carbon electrode used for the direct current (DC) arc-discharge evaporation of carbon. During the process Iijima used a pressurized chamber filled with a gas mixture of 10 Torr methane and 40 Torr argon. Two vertical thin electrodes were installed in the center of the chamber (**Figure 1**). The lower electrode (cathode) contained a small piece of iron in a shallow dip made purposefully to hold iron.

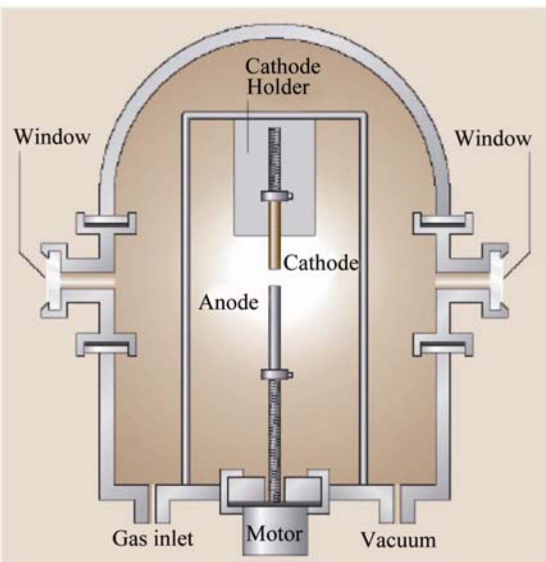

Figure 1. Arc discharge method for CNT.

The arc was generated by running a DC current of 200 A at 20 V between the electrodes. The use of the three components, namely argon, iron and methane, was critical for the synthesis of SWNT. Carbon soot produced as result of arc-discharge settled and nanotubes grew on the iron catalysts contained in negative cathode. The nanotubes had diameters of 1 nm with a broad diameter distribution between 0.7 and 1.65 nm. In a similar process Bethune *et al*. used thin electrodes with bored holes as anodes, which were filled with a mixture of pure powdered metals (Fe, Ni or Co) (catalysts) and graphite. The electrodes were vaporized with a current of 95 - 105 A in 100 - 500 Torr of Helium. SWNT were also produced by the variant of arc-technique by Journet *et al*. [12] as well. In his variant, the arc was generated between two graphite electrodes in a reaction chamber under helium atmosphere (660 mbar). This method also gave large yield of carbon nanotubes. Ebbesen and Ajayan, [13] however, reported large-scale synthesis of MWNT by a variant of the standard arc discharge technique as well.

2.1.2. Laser Ablation Process

In the laser ablation process, a pulsed laser is made to strike at graphite target in a high temperature reactor in the presence of inert gas such as helium which vaporizes a graphite target. The nanotubes develop on the cooler surfaces of the reactor, as the vaporized carbon condenses. A water-cooled surface is also included in the most practical systems to collect the nanotubes (**Figure 2**).

This method was first discovered by Smally and Co-workers at Rive University in 1995 [9]. At the time of discovery they were studying the effect of laser impingment on metals. They produced high yields (>70%) of Single walled Carbon Nanotubes by laser ablation of graphite rods containing small amounts of Ni and Co at 1200˚C. In this method two-step laser ablation was used. Initial laser vaporization pulse was followed by second pulse to vaporise target more rapidly. The two step process minimizes the amount of carbon deposited as soot. Tubes grow in this method on catalysts atoms

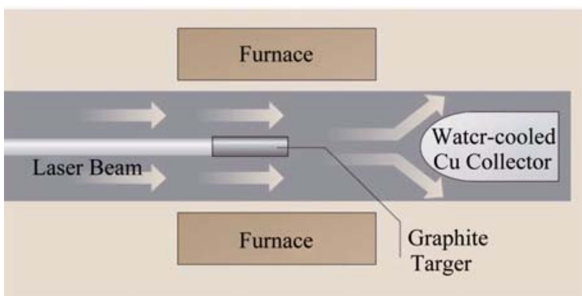

Figure 2. Schematic of laser ablation method for carbon nanotube production.

and continued to grow until to many catalyst atoms aggregate at the end of the tube. The tubes produced by this method are in the form of mat of ropes 10 - 20 nm in diameter and up to 100 micron or more in length. By varying temperature, catalyst composition and other process parameters average diameter and length of carbon naotube could be varied.

2.1.3. Disadvantages of Arc-Discharge and Laser Ablation

Both arc-discharge and laser ablation produces some of the most high quality nanotubes but suffers from following disadvantages which limit their use as large scale industrial processes.

1) They both are energy extensive methods-a large amount of energy is needed to produce arc or laser used for ablation processes. Such a huge amount of energy is not only impossible but also uneconomical for large scale production.

2) Both methods require solid carbon/graphite as target which has to be evaporated to get nanotubes. It is difficult to get such large graphite to be used as target in industrial process which limits its exploitation as large scale process.

3) Both processes grow nanotubes in highly tangled form, mixed with unwanted form of carbon or catlysts. Thus CNTs produced by these processes require purification to get purified and assembled forms. The designing of such refining processes is difficult and expensive.

All the above mentioned factors severely limit the use of both arc-discharge and laser ablation as large scale processes for production of carbon nanotubes.

2.2 Chemical Processes

2.2.1. Chemical Vapor Deposition

In 1996 Chemical vapor deposition emerged as potential method for large scale production and synthesis of carbon nanotubes. This method is capable of controlling growth directions on a substrate and synthesizing a large quantity of carbon nanotubes [14]. In this process a mixture of hydrocarbon gas (ethylene, methane or acetylene) and a process gas (ammonia, nitrogen, hydrogen) is made to react in a reaction chamber on heated metal substrate at temperature of around 700˚C - 900˚C, at atmospheric pressures. CNTs formed as a result of decomposition of hydrocarbon gas and deposit and grow on metal catalyst (substrate). The catalysts particle can stay at the bottom or top of growing carbon nanotube.

The use of the catalyst and preparation of the substrate is one of the most important factors in CVD, as this substrate will define the nature and type of carbon nanotubes formed. The usually substrate material is silicon, but glass and alumina are also used. The catalysts are metal nanoparticles, like Fe, Co and Ni, which can be deposited on substrates by means of electron beam evaporation, physical sputtering or solution deposition. Porous silicon is an ideal substrate for growing self-oriented nanotubes on large surfaces. The nanotube diameter depends on the catalyst particle size, therefore, the catalyst deposition technique should be chosen carefully to yield desired results.

A variant of CVD known as “plasma assisted CVD” is a process in which a plasma is generated during the process. By properly adjusting the geometry of reactor during plasma assisted CVD, it is possible to grow vertically grown carbon naotubes. Without plasma carbon nanotubes produced are usually random gropus just like bowl of spaghetti. However, under certain carefully controlled conditions even in the absence of plasma vertically alighned carbon nanotubes resembling that of forst or carpet can be produced. Recently at University of Califfornia, Berkeley [15] researchers have also reported the production of double walled carbon nanotubes from CVD. Similar success has also been reported at University of California, San Diago [16].

2.2.2. High Pressure Carbon Monoxide Reaction (HiPco®)

This is a unique method developed at Rice University in 1999 for the production of carbon nanotubes [17]. Unlike other methods in which the metal catalysts are deposited or embedded on the substrate before the deposition of the carbon begins, in this method catalyst is introduced in gas phase. Both the catalyst and the hydrocarbon gas are fed into a furnace, followed by catalytic reaction in the gas phase. This method is suitable for large-scale synthesis, because the nanotubes are free from catalytic supports and the reaction can be operated continuously. Usually CO gas is used as hydrocarbon gas which reacts with iron pentacarbonyl, $Fe(CO)_5$ to form SWNT. This process is called HiPco process. SWNT have also been synthesized in a variant of HiPco process in which a mixture of benzene and ferrocene, $Fe(C_5H_5)_2$ reacts in a hydrogen gas flow to form SWNT [18]. In both methods, catalyst nanoparticles are formed through thermal decomposition of organometallic compounds, such as iron pentacarbonyl and ferrocene.

2.2.3 CoMoCAT® Process

Recently an effort has been made at University of Oklahoma [19], to develop a process using Cobalt and Molybdenum catalysts and CO gases. In this method, SWNT are grown by CO disproportionation (decomposition into C and CO_2) in the presence of CoMo Catalyst (specifically developed for the purpose) at 700˚C - 950˚C in flow of pure CO at a total pressure that typically ranges from 1 to

10 atm. This process is able to grow a significant amount of SWNT (about 0.25 g SWNT/g catalyst) in a couple of hours, keeping selectivity towards SWNT better than 80%. The secret of the process is in synergistic effect of Co and Mo. Catalyst is most effective when both metals Co and Mo are present at a time on silica substrate with low Co:Mo ratio. The material produced by the HiPco process yields a much larger number of bands, which indicate a greater variety of diameters than the material produced by CoMoCAT Process. The distribution of diameters produced by the HiPco process reported in the literature is also significantly broader than that of the product obtained from the CoMoCAT process. This process carries strong prospects in it to be scaled up as large scale production process for the production of SWNT.

2.2.4. Advantages of Chemical Processes

These methods have many advantages as compared to forementioned processes.

1) Reaction process and reactor design is simple, reaction is easy to control and manipulate.

2) Raw materials are abundant and available readily in the form of gases.

3) Due to absence of expensive and difficult to produce targets and huge amount of energy needed, process is cheap in terms of unit price.

4) Process is capable of producing CNTs directly onto substrates which ease out the process of further collection and separation and eliminates post refining processes to a large extent. Some refining is required in some cases for further purification.

5) Process is unique for the production of vertically alighned nanotubes. No other process can produce alighned nano tubes.

f. Process can be designed for continuous operation (HiPco) and easily scaled up to large industrial process due to its nature of operation similar to chemical unit operations.

More and more research is underway in the world today for the production of large quantities of high purity carbon nanotubes by chemical vapor deposition process.

Researchers are developing method and designing reactors, which could be utilized as units for large scale production of carbon nanotubes.

2.3 Miscellaneous Processes

Some miscellaneous and relatively less used processes of carbon nanotube production are given below.

2.3.1 Helium Arc Discharge Method

It was reported in 2006 by scientists of NASA's Goddard Space Flight Center that they have developed a simple, safe, and very economical process of Single walled carbon nanotubes production [20]. In this method scientists used a helium arc welding process to vaporize an amorphous carbon rod and then form nanotubes by depositing the vapor onto a water-cooled carbon cathode. This process yields bundles, or "ropes," of single-walled nanotubes at a rate of 2 grams per hour using a single setup. I was claimed that process would produce SWCNT with yield of 70% at a much lower cost as compared to previously achieved yield of 30% - 50% at a cost of approximately $100 per gram. Further it was claimed, as process does not require any metal catalyst no metal particles need to be removed from the final product. Eliminating the presence of metallic impurities results in the SWCNTs exhibiting higher degradation temperatures (650˚C rather than 500˚C) and eliminates damage to the SWCNTs by the purification process.

This process is under discussion for potential use as commercial scale process.

2.3.2. Electrolysis

In this method carbon nanotubes were produced at University of Miskolc by G. Kaptay & J. Sytchev [21] by depositing alkali metals on a graphite cathode from a high-temperature molten salt system. The deposited metallic atoms intercalate into the space between the graphitic sheets and diffuse towards the bulk of the graphite cathode, causing some mechanical stress inside graphite. This stress induces the ablation of separate graphitic sheets, which will turn into carbon nanotubes due to interfacial forces, trying to recombine broken carbon-carbon bonds. Though this method has been reported to yield good quality of carbon nanotubes. It is not scaleable to large scale production method to produce carbon nanotubes.

2.3.3 Flame Synthesis

This method is based on the synthesis of SWNT in a controlled flame environment, that produces the temperature, forms the carbon atoms from the inexpensive hydrocarbon fuels and forms small aerosol metal catalyst islands [22,23]. SWNT are grown on these metal islands in the same manner as in laser ablation and arc discharge. These metal catalyst islands can be made in three ways. The metal catalyst (cobalt) can either be coated on a mesh [22], on which metal islands resembling droplets were formed by physical vapor deposition. These small islands become aerosol after exposure to a flame. The second way is to create aerosol small metal particles by burning a filter paper that is rinsed with a metal-ion (e.g. iron nitrate) solution. The third way is the thermal evaporating technique in which metal powder (e.g. Fe or Ni) is inserted in a trough and heated [23].

In a controlled way a fuel gas is partially burned to gain the right temperature of ~800˚C and the carbon atoms for SWNT production. On the small metal particles the SWNT are than formed. As optimization parameters the fuel gas composition, catalyst, catalyst carrier surface and temperature can be controlled [22]. In the literature found, the yield, typical length and diameters are not stated.

3. Comparison

Below a comparison of three most widely used methods is given (**Table 1**) with respect to their potential to be scaled up as large scale methods for production of carbon nanotubes.

4. Conclusions

Following conclusion can be drawn from above discussion about different methods of carbon nanotubes production.

- Both arc-discharge and laser ablation methods suffer from disadvantages of being expensive and uneconomical methods of production of carbon nanotubes on large scale, despite they yield high quality carbon nanotubes with reasonable high yield.
- Chemical Vapor Deposition is best-suited, economic method of production of high purity Single Walled Carbon Nanotubes (SWNT) on large scale.
- Variants of Chemical Vapor Deposition process such as CoMoCAT® & HiPco® can be scaled up to large scale processes with continuous process & high yield.

Table 1 Comparison of Carbon Nanotube Production Methods.

Process / Property	Arc-discharge	Laser Ablation	Chemical Vapor Deposition
Raw materials availability	Difficult	Difficult	Easy, abundantly available
Energy requirement	High	High	Moderate
Process control	Difficult	Difficult	Easy, can be automated
Reactor design	Difficult	Difficult	Easy and can be designed as large scale process
Production rate	Low	Low	High (CoMoCAT, HiPco)
Purity of product	High	High	High
Yield of process	Moderate (70%)	High (80% - 85%)	High (95% - 99%)
Post treatments requirements (refining etc.)	Require refining	Require refining	No extensive refining required
Process nature (continuous or batch type)	Batch type	Batch type	Continuous
Per unit cost	High	High	Low

- Chemical Vapor Deposition process can also be used for economic production of Double Walled Carbon Nanotubes.
- Miscellaneous processes such as NASA's process still require qualification to be adopted as high scale mass production processes.

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